

Metal Deactivation in Lard¹

S. G. MORRIS, J. S. MYERS, JR., MARY L. KIP, and R. W. RIEMENSCHNEIDER,
Eastern Regional Research Laboratory,² Philadelphia 18, Pennsylvania

421

IN attempting to explain the role of antioxidants, Titoff (1) in 1903 concluded that antioxidants bind up (by complex formation) the positive oxidation catalyst, rendering it inactive and thereby effecting increased resistance to oxidation. He showed that the pro-oxidant effect of copper in the auto-oxidation of dilute solutions of sodium sulfite could be hindered by traces of benzyl alcohol, benzaldehyde, mannite, glycerol, and various phenols. Although these observations did not prove that this hindered oxidation was due exclusively to complexing of metal, his concept was that of metal deactivation rather than a general explanation of the role of antioxidants.

During the past 20 years there has been increasing interest in the effect of metallic contaminants in petroleum products and in fats and oils, and in means of preventing this contamination or in rendering these trace elements ineffective. It is now generally known that copper, cobalt, manganese, and iron in the form of their salts or oxides are powerful promoters of oxidation, and that tin, aluminum, and nickel salts, although far from being inactive, are among the less powerful promoters. Precautions have been taken in plant practice and construction to decrease this contamination by keeping the pumping lines as short as feasible, by eliminating copper-bearing metals in pumps and fittings, and by attempting to keep rust or corrosion of tanks and pipe lines to a minimum. When it is considered however that only one or two parts of copper or 10 to 20 parts of iron per ten million parts of fat or oil may noticeably increase the rate of oxidation or rancidification, it seems probable that such trace contamination could occur despite precautions. Therefore further treatment to inactivate these trace quantities of metals would be of considerable importance. A number of compounds have been patented for use primarily in gasoline, many of which would probably be unsuited for edible fats and oils. Among these are condensation products of ethylene diamine and o-hydroxyacetophenone (2), 2-hydroxyacetophenoxime (3), salicylalaminoguanidine (4), phenyl dihydroxyphosphine (5), lecithin and disalicylal ethylene diamine (6), condensation products of salicylaldehyde and a number of amino acids (7), guanylguanidine (8), stearamido-methylphosphonic acid (9), dihydroxydiazo compounds (10), salicylal glucamine (11), and thiourea (12).

Comparatively little work has been reported on investigations of deactivators for traces of metals in fats and oils. Commercial tannins (13) are effective in the treatment of lard to remove metallic impurities. In this treatment the tannin-metal compounds and excess tannins are removed by filtration. A possible relation of the synergistic effect of certain compounds, when used with antioxidants of the phenolic type, to metal deactivation has been pointed out (14).

Citric acid has been shown (15) to extend considerably the oxidative stability of soybean oil containing iron stearate after natural tocopherols (antioxidants) have been removed by adsorption. Evidence was also presented that certain other polyhydric alcohols and citric acid are metal scavengers. The question as to whether citric acid and these other compounds found to be effective in counteracting the pro-oxidant effect of metals have also a true synergistic antioxidant action has not been satisfactorily settled. Citric acid when used with a phenolic antioxidant however has shown an enhancing effect on the stability of methyl esters of lard which had been distilled in all-glass apparatus and were presumably free of metallic salts (16).

The present paper describes experiments which show the effect of copper, iron, nickel, and tin on the oxidative stability of lard. A series of compounds were evaluated for their metal deactivating power alone, and in combination with antioxidants.

Experimental

The lard used in these experiments was good quality steam-rendered lard. No tests were made to determine whether it was free of metals, but its high stability would indicate that its metal content was very low.

The metal ions were added to the lard in the form of their chloride salts dissolved in alcohol. All the metallic ions were in the "ic" instead of the "ous" form except that of nickel. The chloride salts were preferred to the metallic salts of fatty acids because of their availability and also because they were not subject to rancidity, as were the metallic soaps.

Methods. The modified active oxygen method (AOM) (17) was employed in evaluating stability. The compounds tested as metal deactivators, that were not readily soluble in fat, were incorporated into the lard as an alcoholic solution. The solvent was removed by heating the mixture in a deodorizer at 60° under reduced pressure (18). The metallic chlorides, dissolved in 0.2 cc. of alcohol, were added directly to the lard sample in the aeration tube at the beginning of the test. The alcohol solvent soon evaporated under the conditions of the AOM test. This procedure was used because the metallic salts could not be incorporated satisfactorily into the lard in the same manner as the antimetallic compounds were, owing to rapid formation of peroxides during the removal of solvent.

Results and Discussion

A somewhat arbitrary decision was made as to what concentrations of metal should be used. It was decided to use the lowest concentrations that would reduce the stability of lard to approximately 0.5 to 1 hour. These concentrations were determined by the experiments shown in Table I. Under the conditions of the AOM test the rate of peroxide formation was so great that no significance can be ascribed to the differences in pro-oxidant effect of the metals

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² One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

TABLE I
Effect of Metals on the Stability (AOM) of Lard

Metals	Conc.		Stability
	p.p.m.	Hrs.	
Control (lard A).....	7.0	
Cu.....	10.0	0.3	
Cu.....	5.0	0.3	
Cu.....	1.0	0.4	
Cu.....	0.5	0.5	
Cu.....	0.4	0.5	
Cu.....	0.3	0.5	
Cu.....	0.2	0.8	
Cu.....	0.1	3.2	
Fe.....	20.0	0.3	
Fe.....	10.0	0.3	
Fe.....	5	0.3	
Fe.....	3	0.4	
Fe.....	2	0.5	
Fe.....	1	2.0	
Ni.....	2	1.0	
Control (lard B).....	6.0	
Ni.....	4	1.0	
Ni.....	10	1.0	
Ni.....	20	1.0	
Sn.....	10	3.0	
Sn.....	20	1.0	

within the range of 0.3 to 10 parts per million for copper; 2 to 20 for iron; and 2 to 20 for nickel. The amount of tin required to reduce the stability of the control lard to 1 hour was 20 parts per million. The concentrations chosen were (parts per million); for lard A, Cu 0.2, Fe 2.0, and Ni 2.0; for lard B, Ni 4.0 and Sn 20. For a strictly quantitative comparison of the effects of varying concentrations of these metals, the experiments should be conducted at lower temperatures and preferably by an oxygen absorption method.

The influence of known antioxidants on lard containing these amounts of metals was determined. Table II gives these data. For comparison with the effect of the metals alone it is necessary to refer to Table I. In every instance the effectiveness of the antioxidant was markedly lessened by the metal, although in many instances there was still appreciable antioxygenic effect, since the stability was greater than that of the control lard. The question naturally arises as to whether the antioxidant deactivated the metal, leaving some unreacted antioxidant still functioning, or whether no metal deactivation took place. In the latter case it would be assumed that the metal-catalyzed and non-catalyzed oxidations proceed by the same mechanism, a chain-reaction mechanism ac-

TABLE II
Effect of Metals on Stability of Lard in the Presence of Antioxidants

Antioxidant	AOM Stability in Presence of				
	0.2 p.p.m. ¹ Cu	2.0 p.p.m. ¹ Fe	4.0 p.p.m. ² Ni	20 p.p.m. ² Sn	No metal
	Hrs.	Hrs.	Hrs.	Hrs.	Hrs.
0.01% lauryl gallate	6.5	0.7	21 ³	51
0.02% lauryl gallate	13
0.01% ethyl pyrogallol	35	1	72	18	126
0.02% ethyl pyrogallol	54
0.01% butylhydroxy anisole	7.5	4.2	15	19	22
0.01% mono or diethyl ether of ethyl pyrogallol	1	1	3	4.5	12
0.01% ditertiary butyl-p-cresol	5.5	4.7	8.5	12	25
0.02% ditertiary butyl-p-cresol	9.5	39
0.01% β , 3,4-dihydroxy-phenyl alanine	26	0.4	1.2	2	73
0.01% adrenalin	26	8	83
0.01% phloramine	11	0.7	11	8	35
0.01% methyl phloramine	21	1.5	26	13	54
0.01% JZF ⁴	3.2	0.7	74

¹ Control lard A was used for all experiments with Cu and Fe.

² Control lard B was used for all experiments with Ni and Sn except one.

³ Control lard A was used; 0.2 p.p.m. Ni.

⁴ The chief ingredient was N,N' diphenyl p-phenylene diamine.

cording to modern theory. Similarly, the chain-terminating mechanism of the antioxidant would be the same in the catalyzed and non-catalyzed oxidations. However since the catalyzed reaction takes place at the faster rate, the apparent-efficiency of the antioxidant would be less, as measured by stability units. It is considered unlikely that the antioxidant deactivated the metals in most of these instances because when some of the antioxidants were added in 0.02% concentrations in the presence of metal, the increased stability did not approach that obtained when 0.01% of the antioxidant was added without the metal. For example, ethyl pyrogallol in 0.01% concentration without added metal imparted a stability of 126 hours; with 0.2 parts per million of Cu added, 35 hours; whereas 0.02% ethyl pyrogallol in the presence of the same Cu content gave only 54 hours stability. Further indications that these antioxidants are generally ineffective as metal deactivators are shown by the results in Table IV, which are discussed later.

TABLE III
Evaluation of Some Synergists as Metal Deactivators

Synergist	AOM Stability in Presence of				
	0.2 p.p.m. Cu	0.4 p.p.m. Cu	2.0 p.p.m. Fe	2.0 p.p.m. Ni	No metal
	Hrs.	Hrs.	Hrs.	Hrs.	Hrs.
Control (lard A, Table I)	0.8	0.5	0.5	1.0	7
0.01% ascorbic acid	10	10	0.5	10
0.02% l-ascorbyl palmitate	8	0.3	13
0.024% potassium l-ascorbyl palmitate	11	8.5	10	14
0.01% tartaric acid	4	3	6	7
0.016% potassium tartrate	0.4	0.3	6
0.012% K-acid tartrate	0.4	0.3	7
0.01% citric acid	2.2	1.7	4.5	3.5	7
0.01% phosphoric acid	1.7	3.5	4.7	4.7
0.01% sorbitol	0.5	0.7	7
0.01% mannitol	0.4	0.3	3.2
0.01% lactic acid	0.4	0.5	6

Compounds considered to be synergists were also added to lard containing the concentrations of metals mentioned; Table III shows the results. Addition of ascorbic acid, l-ascorbyl palmitate, and potassium l-ascorbyl palmitate brought about substantial recovery from the effects of added copper, but the first two were completely ineffective against iron; the third was effective against copper, iron, and nickel. Citric acid was appreciably more effective against iron and nickel than against copper.

Some antioxidants in general were considerably less effective in the presence of metals and certain compounds having a reputation as synergists appeared to deactivate metals, it was of further interest to determine the effect of antioxidant and synergist in the presence of metals. Results of these experiments (Table IV) support the previous conclusion that these synergists deactivate the metal. When an antioxidant is also present, its effectiveness approaches that obtained when no metal is present. Although these results indicate strongly that compounds such as ascorbic acid and citric acid function as metal deactivators it is not implied that their synergistic action with antioxidants is exclusively metal deactivation.

In view of the fact that synergistic activity has been attributed to certain amino acids and amines

TABLE IV
Evaluation of Synergists as Metal Deactivators in the Presence of 0.01 Per Cent Lauryl Gallate in Lard A

Synergist	AOM Stability in Presence of				
	0.2 p.p.m. Cu	0.4 p.p.m. Cu	2.0 p.p.m. Fe	2.0 p.p.m. Ni	No Metal
None	Hrs.	Hrs.	Hrs.	Hrs.	Hrs.
0.01% ascorbic acid	6.5	0.7	21	51
0.01% l-ascorbyl palmitate	60	59	0.7	41	63
0.024% potassium l-ascorbyl palmitate	67	62	0.3	50	68
0.01% citric acid	71	49	69	74
0.01% phosphoric acid	33	26	40	49	56
	29	1.5	31	59

and that a number of amino compounds have been patented as metal deactivators for petroleum products, some attention was given to testing a series of compounds of this type. The following amino acids and other amino compounds were tested as metal deactivators for copper and iron: proline, methionine, phenylalanine, p-aminosalicylic acid, 2,5-dimethyl piperazine, 2-amino-2-methyl-1-propanol, 2-amino-2-methyl-1,3-propandiol, tris (hydroxymethyl) amino-methane, vanillin amine, and vanillin amine hydrochloride. Most of them were also tested against nickel and tin. None showed any appreciable effectiveness as metal deactivators.

Summary

A number of compounds, including known synergists, amino acids, and amines, have been evaluated as deactivators for copper, iron, nickel, and tin in lard. Some were effective in deactivating copper but

were relatively poor for iron. One compound was better for iron than for copper.

Ascorbyl palmitate, potassium ascorbyl palmitate, and ascorbic, tartaric, citric, and phosphoric acids were the most effective. This deactivation may in part explain the synergistic effect of these compounds with phenolic antioxidants.

The more powerful antioxidants however are generally poor metal deactivators, and in the presence of traces of metallic pro-oxidants become relatively ineffective unless metal deactivators are also added.

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